Short communication

Preparation of graphene-supported platinum nanoparticles in aqueous solution by femtosecond laser pulses for methanol oxidation

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HIGHLIGHTS

- $PtCl_6^{2-}$ and graphene oxide was reduced simultaneously by femtosecond laser pulses.
- This work exhibited higher electrocatalytic ability than other methods.
- This method is potential to synthesize other metals on graphene for fuel cells.

ARTICLE INFO

ABSTRACT

A simple and rapid approach for the deposition of platinum (Pt) nanoparticles onto surface of graphene in aqueous solution without reducing agents by femtosecond laser pulses is demonstrated. The formation of graphene-supported Pt in aqueous solution is confirmed by a variety of means such as ultraviolet−visible absorption spectroscopy, transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. Graphene oxide and $PtCl_6^{2-}$ are simultaneously reduced and Pt nanoparticles can be deposited on the surface of graphene. The presence of Pt on graphene is further confirmed by cyclic voltammetry. The value of electrochemically active surface area of the prepared graphene-supported Pt (58.9 m^2 g^{-1}) is higher than most previously reported preparation methods for graphene-supported Pt. For the electrochemical oxidation of methanol, the prepared graphene-supported Pt exhibits a mass activity of 295 mA mg^{-1} at 0.669 V, which was higher than commercial Pt catalyst and graphene-supported Pt prepared by electrochemical method.

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1. Introduction

Platinum (Pt) nanoparticles are proven to be very useful for the enhancement of electrochemical oxidation of methanol. Many factors such as Pt particle size and distribution [1–3] and preparation methods [1,4,5] can affect the electrocatalytic activity towards electrochemical oxidation of methanol. Pt nanoparticles are deposited onto a variety of carbon supports such as carbon black, carbon nanotube, and graphene in order to improve its electrocatalytic ability [6,7]. Graphene has been extensively studied because it displays high aspect ratio, excellent electrical conductivity, outstanding mechanical strength, and good chemical stability [8–12]. It has been shown to exhibit excellent characteristics in various applications such as fuel cells [13–15] and supercapacitors [16–18].

To date, much research has been developed to the preparation of graphene-supported Pt. There are mainly three approaches to grow Pt nanoparticles onto the surface of graphene. One is to attach Pt precursor onto the surface of graphene oxide (GO) followed by the reduction of Pt precursor and GO with chemical agents [19]; another is to reduce GO nanosheets first and then deposit Pt nanoparticles on the graphene [20]; the other is one-step method for growth of Pt nanoparticles on graphene. Among these methods, the one-step synthesis procedure of graphene-supported Pt to increase the electrocatalytic ability seems very attractive because of its simplicity. The strategies of single step preparation of graphene-supported Pt can be roughly classified as solution-phase reduction [13,21,22], thermal decomposition [23], microwave-assisted method [24], and electrochemical deposition [25]. In the former one, a reducing agent such as ethylene glycol was introduced into a solution containing Pt precursor and GO. Here we report a rapid, straightforward, and green one-step procedure for the fabrication of graphene-supported Pt under mild condition.

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Recently, femtosecond laser pulses has attracted much attention to fabricate nanostructured materials because the laser pulse duration is shorter than the electron cooling time and heat diffusion into target materials can be minimized [26]. Metal surfaces under liquid water environments have been converted with controlled femtosecond laser pulses into nanoparticles and nanomaterials [27]. In this paper, we demonstrate an efficient approach for the preparation of graphene-supported Pt in aqueous solution by femtosecond laser pulses beginning with $PtCl_6^{2-}$ and GO. Importantly, the one-step synthesis of Pt nanoparticles on graphene is achieved without the addition of any poisonous reducing agent and surfactant. The prepared graphene-supported Pt for the electrochemical oxidation of methanol was described and discussed.

2. Experimental

2.1. Reagents

Potassium hexachloroplatinate (IV) (K_2PtCl_6) was obtained from Showa. Methanol (CH_3OH) and concentrated sulphuric acid (H_2SO_4) were obtained from Fluka. The commercial Pt catalyst (20 wt% Pt on carbon black Vulcan XC-72) was purchased from Premetek. All solutions were prepared with demineralized and filtered water of resistivity of not less than 18 MΩ cm which was taken from a Milli-Q water purification system (Milli-Q, USA).

2.2. Apparatus

Ultraviolet (UV)–visible absorption spectra were obtained with a Lambda 25 UV–visible spectrophotometer (Perkin Elmer, USA). Transmission electron microscopy (TEM) images of GO and graphene-supported Pt were recorded on a JEM-2010 (JEOL, Japan). X-ray diffraction (XRD) patterns were recorded using a D8 Discover X-ray diffractometer with Cu Kα radiation (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) measurements were obtained on a Phi 5000 VersaProbe Scanning ESCA Microprobe using Al Kα radiation (Ulvac-Phi, Japan). Electrochemical measurements were performed with an Autolab PGSTAT30 Electrochemical Analyzer (Eco Chemie, Netherlands). A conventional three-electrode system was carried out with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode.

2.3. Preparation of graphene-supported Pt in aqueous solution by femtosecond laser pulses

GO was synthesized from graphite powder by a modified Hummers method [28]. 10 mg of GO was dispersed in 10 mL deionized water and ultrasonication for about 15 min to form a uniform GO solution. A total of 4 mL of 1 mg mL^{-1} GO and 1 mM $PtCl_6^{2-}$ aqueous solution was kept in a $10 \times 10 \times 45$ mm^3 quartz vessel. The high intensity femtosecond laser pulses generated by a regenerative amplified mode-locked Ti:Sapphire laser (SPIT FIRE, Spectra-Physics) with central wavelength at ~800 nm, pulse duration of ~120 fs, repetition rate of 1 kHz, and laser intensity 1.5×10^{15} W cm^{-2} were introduced into the vessel perpendicular to its surface and tightly focused in the solution using an aspheric lens with a focal length of 8 mm and a numerical aperture of 0.5 (Thorlabs C240TME-B). After the irradiation, the product was rinsed and characterized by UV–visible spectroscopy, TEM, XPS, and XRD. For comparison, Pt was electrochemically deposited on a graphene modified glassy carbon electrode at a constant potential of −0.4 V versus Ag/AgCl in 0.1 M phosphate buffer solution containing 1 mM $PtCl_6^{2-}$ for 500 s. The Pt loadings of graphene-

supported Pt prepared by femtosecond laser and electrochemical reduction were 14 and 16 wt%, respectively which were determined by thermogravimetric analysis (not shown).

2.4. Preparation of graphene, carbon black-supported Pt, and graphene-supported Pt modified glassy carbon electrodes

Before the surface modification, the 3 mm bare glassy carbon electrode was polished with 0.3 and 0.05 μm alumina slurries and washed with deionized water several times. The graphene, carbon black-supported Pt, and graphene-supported Pt modified glassy carbon electrodes were prepared by casting 8 μL aliquot of graphene (1 mg mL^{-1}), carbon black-supported Pt (1 mg mL^{-1}), and graphene-supported Pt (1 mg mL^{-1}) solution on glassy carbon electrodes and the solvent was allowed to evaporate at room temperature in the air.

3. Results and discussion

A mixture of K_2PtCl_6 and GO in aqueous solution was subjected to a femtosecond laser pulse irradiation with different times. The simultaneous reduction processes of $PtCl_6^{2-}$ and GO in aqueous solution by femtosecond laser pulses were monitored by UV–visible absorption spectroscopy. The UV–visible spectra of $PtCl_6^{2-}$ and GO in aqueous solution before and after the irradiation of femtosecond laser pulses with different times are shown in Fig. 1. Along with the reduction process of $PtCl_6^{2-}$ and GO by femtosecond laser pulses, the absorption peak at 201 nm, characteristic of $PtCl_6^{2-}$ in aqueous solution [29], decreased gradually with the increase of femtosecond laser pulse irradiation time (1–10 min) and disappeared completely after 20 min. At the same time, a broaden absorption peak can be observed around 257 nm with a femtosecond laser pulse irradiation time of 20 min. The change in colour from light brown to dark brown to black can be seen in the inset of Fig. 1 as the reduction of $PtCl_6^{2-}$ and GO in aqueous solution proceeded. Slow setting of the prepared graphene-supported Pt can be observed with a femtosecond laser pulse irradiation time of 20 min. Mild sonication of the graphene-supported Pt facilitated its resuspension. The disappearance of the characteristic peak of $PtCl_6^{2-}$ at 201 nm and the red shift of the absorption peak of GO with the increase of femtosecond laser pulse irradiation time are evident of the simultaneous reduction of $PtCl_6^{2-}$ and GO in aqueous solution.
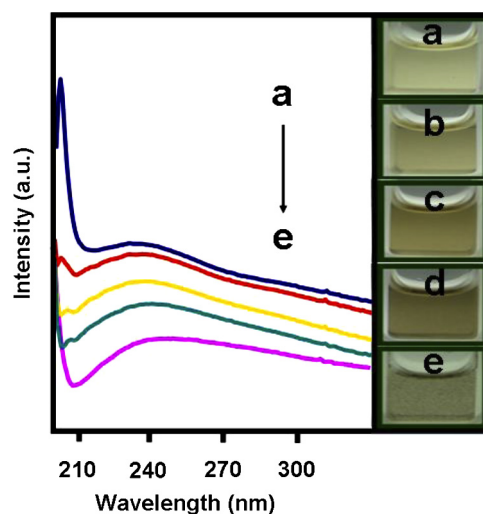

Fig. 1. UV–visible spectra of $PtCl_6^{2-}$ and GO in aqueous solution with femtosecond laser pulse irradiation time of (a) 0, (b) 1, (c) 5, (d) 10, and (e) 20 min.

The direct evidence of the formation of Pt nanoparticles on the surface of graphene was investigated by TEM. The TEM images of GO sheet and graphene-supported Pt are shown in Fig. 2a and b, respectively. The presence of oxygenated functional groups on the GO surface are likely to provide binding and nucleation sites for Pt nanoparticles [30]. The exfoliated single sheet of GO in Fig. 2a can provide a relatively large area on which to anchor the Pt nanoparticles. The distribution of the Pt nanoparticles (black dots) on the 2-D sheet of carbon can be observed in Fig. 2b. Pt nanoparticles uniformly covered on the surface of the graphene sheet. The sizes of the Pt nanoparticles are in the range of 3−6 nm. Furthermore, there were no dissociated Pt nanoparticles seen out of the graphene in Fig. 2b, indicating Pt nanoparticles are extensively assembled on the graphene sheets.

XRD was employed to confirm the reduction of $PtCl_6^{2-}$ and GO in aqueous solution after the irradiation of femtosecond laser pulses.
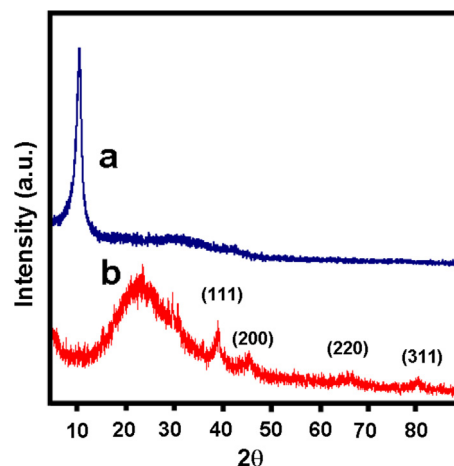

Fig. 3. XRD patterns of (a) GO and (b) graphene-supported Pt.

The XRD patterns of GO and graphene-supported Pt are shown in Fig. 3a and b, respectively. As can be seen from Fig. 3a, there was one major peak at $2\theta = 9.6°$ with d-spacing of 8.57 Å, resulting from the insertion of oxygen-containing functional groups between GO sheets [23]. The peak at $2\theta = 9.6°$ of GO disappeared at graphene-supported Pt, indicating the partial removal of oxygenated functional groups on GO after the irradiation of femtosecond laser pulses. The broad diffraction peak at about $2\theta = 24.1°$ at the graphene-supported Pt (Fig. 3b) could be attributed to the short-range order in stacked carbon sheets [13,23]. The graphene-supported Pt showed diffraction peaks at 39.9° for Pt (111), 46.3° for Pt (200), 67.7° for Pt (220), and 81.4° for Pt (311) [13]. These results confirm that the Pt precursor ($PtCl_6^{2-}$) has been reduced to face-centred cubic Pt by femtosecond laser pulses. The diffraction peak for Pt (111) was used to estimate the Pt nanoparticle size. The average Pt nanoparticle size on graphene calculated by Scherrer equation was 5.0 nm, which is consistent with the TEM results.

XPS was also performed for a more detailed characterization of the chemical bonding at the graphene-supported Pt fabricated by femtosecond laser pulses. The XPS spectra of GO and graphene-supported Pt are shown in Fig. 4a and b, respectively. From the graphene-supported Pt curve, the appearances of Pt peaks in the XPS spectrum for graphene-supported Pt indicate the deposition of Pt nanoparticles on the graphene. The XPS C 1s spectrum of GO and graphene-supported Pt in Fig. 4 shows three peaks at 284.6, 286.3, and 288.1 eV, attributable to C−C, C−O, and C=O bonds,
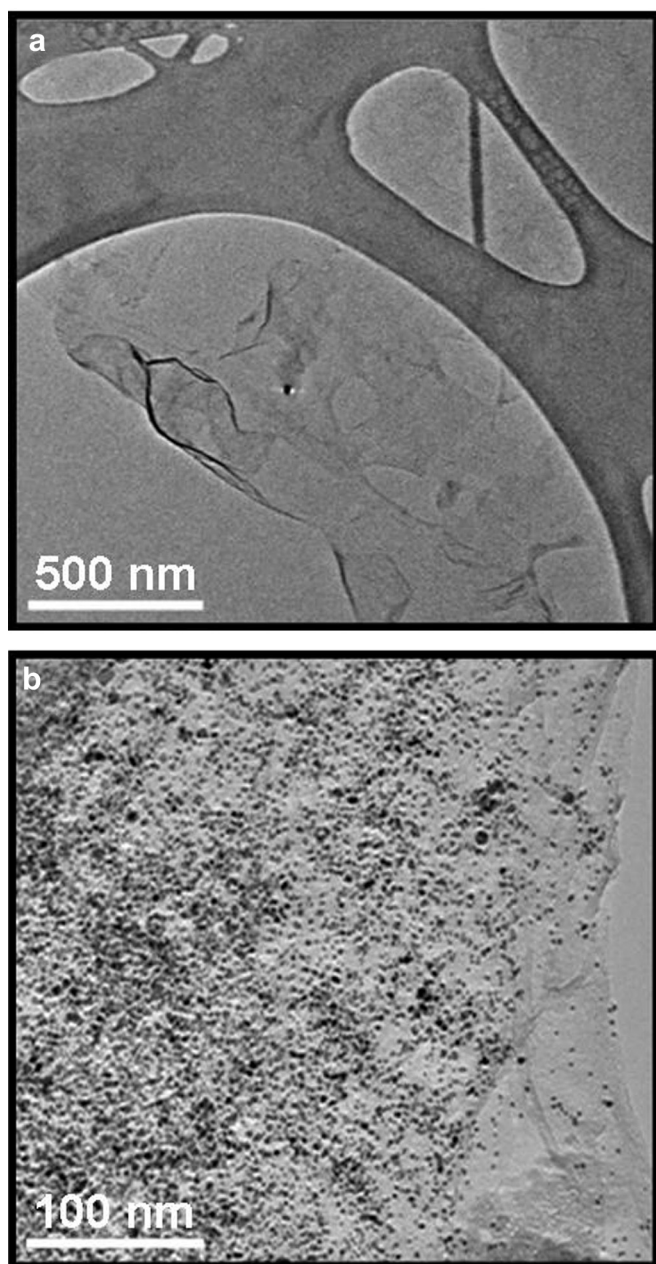

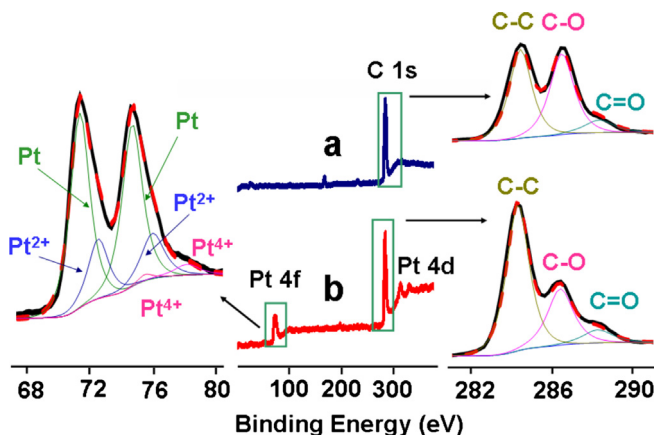**Fig. 2.** TEM images of (a) GO and (b) graphene-supported Pt.

Fig. 4. XPS patterns of (a) GO and (b) graphene-supported Pt.

respectively. As expected, the intensities of C—O and C=O functionalities decreased and C—C increased for the graphene-supported Pt. These results imply that considerable deoxygenation occurred for GO in aqueous solution by the irradiation of femtosecond laser pulses. Meanwhile, the XPS Pt 4f spectrum of graphene-supported Pt in Fig. 4b can be fitted by three doublets at about 71, 74.3 (Pt^0), 72.2, 75.6 (Pt^{2+}), and 75.1, 77.8 eV (Pt^{4+}). The XPS Pt 4f spectrum of graphene-supported Pt reveals that metallic Pt^0 is the major species (>73%) in the graphene-supported Pt with a smaller amount of oxidized Pt species (<27%). These results are in good agreement with the UV—visible absorption spectroscopy, TEM, and XRD studies, which show that the $PtCl_6^{2-}$ and GO in aqueous solution was reduced simultaneously by the irradiation of femtosecond laser pulses. All the results validate the effectiveness of using femtosecond laser pulses in producing graphene-supported Pt in aqueous solution.

The presence of Pt on graphene is further confirmed by cyclic voltammetry. Cyclic voltammograms in 0.5 M H_2SO_4 solution saturated by N_2 for graphene, carbon black-supported Pt, graphene-supported Pt prepared by electrochemical reduction, and graphene-supported Pt prepared by femtosecond laser modified glassy carbon electrodes are shown in Fig. 5a, b, c, and d, respectively. There is no noticeable hydrogen absorption and desorption is observed for graphene in Fig. 5a. In contrast, graphene-supported Pt show the characteristic hydrogen absorption and desorption on Pt between 0 and −0.2 V (Fig. 5c and d), confirming the presence of Pt on graphene. The H^+ ions are reduced to hydrogen atoms and then are adsorbed on the Pt electrode surface at negative scan. In the reverse scan, the adsorbed hydrogen is desorbed resulting in the anodic current. Electrochemically active surface area (ECSA) provides important information related to the number of available active sites. The ECSA due to hydrogen desorption can be obtained according to the Eq. (1) [31],

$$ECSA\left[cm^2g_{Pt}^{-1}\right] = \frac{charge\left[Q_H, \mu C\ cm^{-2}\right]}{210\left[\mu C\ cm^{-2}\right] \times electrode\ loading\left[g_{Pt}\ cm^{-2}\right]} \tag{1}$$

where Q_H is the integrated area under the desorption peak in Fig. 5. The ECSAs of carbon black-supported Pt, graphene-supported Pt prepared by electrochemical reduction, and graphene-supported Pt prepared by femtosecond laser were determined to be 15.3, 31.2, and 58.9 $m^2\ g^{-1}$, respectively. The
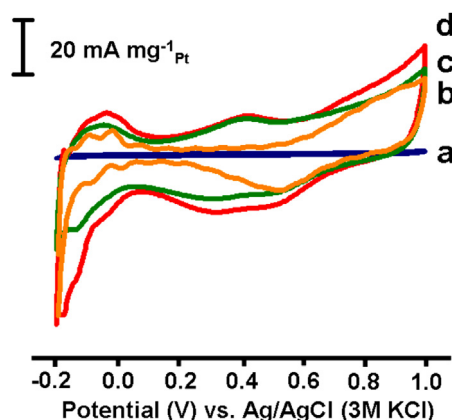
value of ECSA of graphene-supported Pt prepared by femtosecond laser in this work is higher than those of graphene-supported Pt fabricated by chemical and thermal reductions (25.9–44.6 $m^2\ g^{-1}$) [13,21–23]. This result demonstrates that the simultaneous reduction of $PtCl_6^{2-}$ and GO by femtosecond laser pulses increases the available surface area for the electrocatalytic reaction. This larger ECSA is a greater advantage for any electrocatalytic application. The cyclic voltammograms of graphene, carbon black-supported Pt, graphene-supported Pt prepared by electrochemical reduction, and graphene-supported Pt prepared by femtosecond laser modified glassy carbon electrodes in 1 M CH_3OH + 0.5 M H_2SO_4 aqueous solution are shown in Fig. 6,a, b, c, and d respectively. No peak current of methanol oxidation is observed in Fig. 6a, which indicates that the graphene has no electrocatalytic activity towards methanol oxidation. On the contrary, two peaks of methanol oxidation could be observed in Fig. 6b, c, and d at the carbon black-supported Pt and graphene-supported Pt modified electrodes. The peak potentials were 0.669 and 0.492 V for the forward and backward scans, respectively. Tong et al. demonstrated that the forward and backward peak currents shared the same chemical origin and were directly associated with the oxidation of adsorbed methanol [32]. Higher anodic peak currents are observed at the graphene-supported Pt prepared by femtosecond laser. It indicates that the graphene-supported Pt prepared by femtosecond laser exhibits higher electrocatalytic activity than the commercial Pt catalyst and the graphene-supported Pt prepared by electrochemical reduction. The mass activities of carbon black-supported Pt, graphene-supported Pt prepared by electrochemical reduction, and graphene-supported Pt prepared by femtosecond laser were determined to be 111, 249, and 295 mA mg^{-1}, respectively. The mass activity of the graphene-supported Pt prepared by femtosecond laser is higher than those of graphene-supported Pt prepared by microwave-assisted reduction (16.53–46.43 mA mg^{-1}) [24] and electrochemical method (195 mA mg^{-1}) [25]. It is noteworthy that higher ECSA and mass activity of graphene-supported Pt than this work can be obtained with a formic acid reduction method[33]. The advantage of the preparation of graphene-supported Pt in aqueous solution by femtosecond laser pulses is no reducing agent used during the reduction process. The ratio of the forward oxidation peak current to the reverse peak current is 1.45, suggesting that methanol molecules can be effectively oxidized on the prepared graphene-supported Pt.
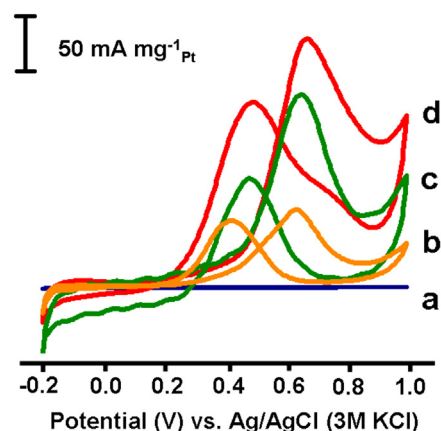

Fig. 5. Cyclic voltammograms of 0.5 M H_2SO_4 aqueous solution at (a) graphene, (b) Carbon black-supported Pt, (c) graphene-supported Pt prepared by electrochemical reduction, and (d) graphene-supported Pt prepared by femtosecond laser modified glassy carbon electrodes. Scan rate: 50 mV s^{-1}.

Fig. 6. Cyclic voltammograms of 1 M CH_3OH + 0.5 M H_2SO_4 aqueous solution at (a) graphene, (b) carbon black-supported Pt, (c) graphene-supported Pt prepared by electrochemical reduction, and (d) graphene-supported Pt prepared by femtosecond laser modified glassy carbon electrodes. Scan rate: 50 mV s^{-1}.

4. Conclusions

We have successfully demonstrated a facial one-step procedure for the preparation of graphene-supported Pt by the irradiation of femtosecond laser pulses in an aqueous solution containing GO and $PtCl_6^{2-}$. GO and $PtCl_6^{2-}$ are simultaneously reduced and Pt nanoparticles can be deposited on the surface of graphene. The prepared graphene-supported Pt modified electrode exhibits higher electrocatalytic ability towards the electrochemical oxidation of methanol than the commercial Pt catalyst and the graphene-supported Pt prepared by electrochemical method. It indicates that femtosecond laser pulse is a good candidate for the preparation of high performance catalyst. The graphene-supported Pt can be fabricated rapidly and control easily by using femtosecond laser pulses. This methodology has a promising potential application to synthesize other metals or alloys of Pt nanoparticles on graphene for direct methanol fuel cells.

Acknowledgements

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